Electron Spin Resonance Spectra of Four-, Five-, and Six-co-ordinate Cobalt(II) Isonitrile Complexes, and of the Pentacyanocobaltate(II) Ion

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E.s.r. spectra, taken at *X*- and *Q*-band, are presented for solutions at 293°K, and glasses at 77 and 150°K, of a series of low spin cobalt(II) isonitrile complexes $Co(CNR)_6^{2+}$, $Co(CNR)_5^{2+}$, $Co(CNR)_4^{2+}$, and $Co(CNR)_4X_2^{2+}$ (X = water, pyridine, or solvent). The spectra of the $Co(CN)_5^{3-}$ ion were also measured in methanol, and in water by a rapid quenching technique. The symmetry of these complexes is C_{4v} or D_{4h} [although the $Co(CN)_5^{3-}$ ion may have C_{2v} symmetry]; the unpaired electron is in the $|0\rangle$ orbital. The value of $g_\perp$ decreases from the four- > five- > six-co-ordinate complex, and this may probably be interpreted in terms of a simple geometry change about the cobalt. From a comparison of the glass and the solution spectra, the components of the hyperfine coupling *A*, and *B*, have opposite signs, thus κ values for the cobalt are calculated (*ca.* 0·2 for the six-, and 0·05—0·1 for the five-co-ordinate ions). The lack of ^{59}Co hyperfine splitting in the spectra of the five-co-ordinate ions in solution may be due to a rapid change from square pyramidal-trigonal bipyramidal geometry. The spectra of the tetrakis(isonitrile) cobalt(II) dihalides show that the contributions from $\zeta_{\sigma\pi}$ dominate the *g* values, in agreement with an electron being in the $|0\rangle$ orbital. Electron delocalisation on the halogen increases as Cl < Br < I.

Cobalt(II) forms low-spin complexes with alkyl and aryl isonitriles. The most stable of these are the five-co-ordinate complexes; however in the presence of an excess of the ligand a six-co-ordinate complex has been detected.[1,2] The four-co-ordinate complex has only been previously reported as the halide adduct $Co(CNR)_4X_2$ (X = Cl, Br, or I); conductivity data have shown that these ionise in aqueous and alcohol solutions.[3] It does not seem possible to prepare $Co(CNR)_4(ClO_4)_2$ since these rapidly disproportionate to the five-co-ordinate ion in suitable solvents.

There has been considerable interest in the structure of the five-co-ordinate ions $Co(CNR)_5^{2+}$ and $Co(CN)_5^{3-}$ which may have either a trigonal bipyramidal (D_{3h}) or a square pyramidal (C_{4v}) structure. If they have the latter form it is also possible that a solvent molecule is co-ordinated in the sixth position. Owing to the stereochemical non-rigidity of five-co-ordinate systems [4] it is further possible that both species exist in solution in some form of dynamic equilibrium. In the solid state it has been established that there is a further water molecule either co-ordinated loosely or incorporated into the crystal lattice of $(C_6H_5NC)_5Co(ClO_4)_2$.[5] The e.s.r. spectrum of the $Co(CN)_5^{3-}$ ion in ethylene glycol–water glasses at 77°K indicates that this species has C_{4v} symmetry.[6]. In the solid state the alkyl isonitriles dimerise to form the ion $Co_2(CNR)_{10}^{4+}$, which is diamagnetic and has a Co–Co bond, giving both cobalt atoms octahedral co-ordination.[7] However, the solution structures of the five-co-ordinate species remain an enigma, in particular there is a question as to whether a molecule of solvent can be co-ordinated in the sixth position. Recent papers have presented evidence that in solutions containing cobalt(II) and cyanide or isonitrile ligands (L), the main complex is $CoL_5(H_2O)$.[2,8] Also complexes of the type $[Co(CNR)_5I]ClO_4$ and $Co(CNR)_6^{2+}$ have been reported.[1-3] Co-ordination of a group in the sixth position is therefore possible. However, kinetic evidence, based on the mechanism of oxidation of $Co(CN)_5^{3-}$ by various complexes $Co(NH_3)_5X^{n+}$,[9] suggests that there is no water co-ordinated in the sixth position in this case. Since $Co(CN)_6^{3-}$ is formed by an outer-sphere oxidation of $Co(CN)_6^{4-}$ (which is present in small amounts in equilibrium with $Co(CN)_5^{3-}$ in the presence of an excess of cyanide), the presence of $Co(CN)_5(H_2O)^{3-}$ would be expected to lead to the formation of $Co(CN)_5(H_2O)^{2-}$. This is not formed in any appreciable amount; although it is possible that the oxidation of the $Co(CN)_5(H_2O)^{3-}$ is kinetically slow compared with the competing reactions, it is not obvious why this might be.

An e.s.r. study of the systems has therefore been carried out to try and resolve the situation.

EXPERIMENTAL

Alkyl and aryl isonitriles were prepared by dehydration of the corresponding *N*-alkyl and *N*-aryl formamide in a base solution with a suitable dehydrating agent.[10] The cobalt(II) complexes were then prepared by reaction of cobalt(II) salt in ethanol with the appropriate isonitrile. The alkyl isonitrile complexes precipitated as red dimeric $[Co(CNR)_5]_2(ClO_4)_4$. Penta(phenyl isonitrile)cobalt(II) perchlorate precipitated as blue-green crystals. The tetrakis(isonitrile)cobalt(II) dihalides all precipitated in their paramagnetic forms; [3] some difficulty was found in preparing $Co(CNR)_4Cl_2$ complexes, the $[Co(CNR)_4][CoCl_4]$ complex being more readily precipitated. The $Co(CNR)_4F_2$ complexes could not be prepared by this method. The complexes were recrystallised from methylene chloride–light petroleum, or from alcohol.

The yellow form of $Co(CNPh)_5(ClO_4)_2$ was prepared *in*

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[1] A. Sacco and M. Freni, *Gazzetta*, 1959, **89**, 1800.

[2] J. M. Pratt and P. R. Silverman, *J. Chem. Soc.* (*A*), 1967, 1286.

[3] L. Malatesta, *Prog. Inorg. Chem.*, 1959, **1**, 283.

[4] E. L. Muetterties and R. A. Schumn, *Quart. Rev.*, 1966, **20**, 245.

[5] J. M. Pratt and P. R. Silverman, *Chem. Comm.*, 1967, 117.

[6] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3356.

[7] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 1965, **4**, 318.

[8] J. M. Pratt and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1967, 1291.

[9] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 1963, **85**, 2517; J. P. Birk and J. Halpern, *ibid.*, 1968, **90**, 305.

[10] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offerman, *Angew. Chem.*, 1965, **4**, 472.

situ by vacuum pumping (*ca.* 10^{-4} mm.) of a sample of the blue compound in the e.s.r. tube before the solvent was distilled on. Methylene chloride was dried over Linde 4 Å molecular sieves and vacuum distilled several times. Methanol was distilled from magnesium methoxide and redistilled *in vacuo*. The e.s.r. spectra of the five-co-ordinate complexes were measured in silica tubes under vacuum. When working under anhydrous conditions the tubes were flamed out under vacuum. Concentrations of the cobalt complex were *ca.* 10^{-3}M. Spectra were measured for the (assumed) $Co(CNR)_6^{2+}$ complexes by distilling the pure isonitrile on dry cobalt chloride *in vacuo* and measuring the spectra as rapidly as possible, firstly at 77°K and then in solution at room temperature. Satisfactory spectra from phenyl isonitrile solutions could only be obtained at 77°K because of the extremely rapid decomposition (to a brown solid which did not show an e.s.r. spectrum). The $Co(CNR)_6^{2+}$ samples were deep yellow in colour, a transient purple colour being observed when the solution was initially made up. The spectra of the $Co(CNR)_4X_2$ complexes were studied in methylene chloride, benzene, acetone, ethanol, and methanol. The resolution of the component lines depends on the solvent viscosity and to a lesser extent the concentration. However the *A* and *g*-values did not appear to depend on concentration within the accuracy of measurements (±0·5 G in *A* and ±0·002 in g). The alkyl isonitrile complexes $Co(CNR)_4Cl_2$ were only sparingly soluble in most organic solvents; their e.s.r. spectra show that they disproportionate in alcohols very easily to form the $Co(CNR)_5^{2+}$ complexes.

For all the complexes, $Co(CNR)_4X_2$, the values of both *g* and *A* depend on both the solvent and the ligand. It is likely that these variations are due to changes in the linewidths of the components rather than to any intrinsic differences. Changes in the linewidths will also effect the peak-to-peak intensity of the components. The best resolved spectra were obtained in methylene chloride and in benzene solution.

Spectra for the $Co(CN)_5^{3-}$ ion were obtained in two ways. (*a*) Various amounts of dry cobalt perchlorate and sodium cyanide with Co : CN ⩾5M were weighed into an e.s.r. tube which was then vacuum pumped for 24 hr., when methanol was distilled onto the solids. Spectra were run at room temperature and at 77°K. The methanol forms a good glass and the $Co(CN)_5^{3-}$ does not dimerise under these conditions.

TABLE 1

Analytical data for the complexes

	Found				Required			
	C	H	N	X	C	H	N	X
$Co_2(CNMe)_{10}(ClO_4)_2$	26·04	3·53	14·91	14·97	25·93	3·26	15·12	15·32
$Co_2(CNEt)_{10}(ClO_4)_2$	33·83	4·79	13·24	13·45	33·76	4·73	13·13	13·30
$Co(CNPh)_5(H_2O)(ClO_4)_2$ Blue-green	53·19	3·44	8·84	9·04	53·11	3·46	8·84	8·96
$Co(CNEt)_4Cl_2$	41·74	6·33	16·62		41·52	5·76	16·00	
$Co(CNEt)_4Br_2$	32·81	4·73	12·7		32·81	4·59	12·75	
$Co(CNEt)_4)I_2$	27·03	3·98	10·66		27·03	3·78	10·50	
$Co(CNMe)_4Cl_2$	32·09	4·22	17·73	23·24	32·7	4·11	19·05	24·15
$Co(CNC_7H_7)_4Br_2$	56·24	4·31	8·37	23·45	55·90	4·11	8·15	23·25
$Co(CNC_7H_7)_4I_2$	49·22	3·71	7·23	32·75	49·18	3·61	7·17	32·48
$Co(CNC_6H_{11})_4Br_2$	52·06	6·98	8·21	25·20	51·30	6·77	8·54	24·39
$Co(CNC_6H_{11})_4I_2$	45·05	6·12	7·37	32·14	44·87	5·92	7·47	33·85

X = Halogen.

(*b*) The $Co(CN)_5^{3-}$ ion (5×10^{-3}M) was prepared in 3M-sodium cyanide solution under nitrogen in a syringe fitted with a Polythene nozzle (0·1 mm. i.d.). This solution was squirted rapidly into isopentane at 165°K in a specially designed e.s.r. tube.[11] Under these conditions sufficient of the $Co(CN)_5^{3-}$ monomer was frozen in the ice for an e.s.r. spectrum to be obtained. Ordinary freezing of an aqueous solution merely results in complete dimerisation. The experiment was repeated using 2·5M-sodium perchlorate and a Co : CN ratio of 1 : 5M when the monomer spectrum was again obtained. The monomer cannot be quenched from aqueous solution in the absence of a strong electrolyte such as sodium perchlorate.

E.s.r. spectra were measured on a Varian V 4502 15 spectrometer at 100 kc. sec.$^{-1}$. field modulation. A reference was provided either by a sample of diphenylpicrylhydrazyl (DPPH) ($g = 2·0037$) or of Fremy's salt (solution) ($g = 2·0055$, $A = 26·1$ G) in a dual cavity arrangement. The Klystron power level was normally operated at 10dB attenuation and the modulation amplitude kept ⩽500 (Varian V 4560). All spectra were independent of these controls up to these levels. For the spectra measured at *Q*-band it was found that with the experimental arrangement provided by Varian the lowest temperature at which spectra could be measured was 150°K and that this temperature was not maintained. Thus the probe typically showed a temperature change from 148—161°K over 40 min. as measured by a copper constantan thermocouple. Temperatures <140°K could only be obtained with the complete loss of the cavity node, probably because the cavity filled with liquid nitrogen.

The ligand-field calculation was carried out on an Elliott 503 computer (Figure 6 shows a replica of a graph plot from the computer).

Analytical data are shown in Table 1.

RESULTS

$Co(CNR)_6^{2+}$.—(Figure 1, Table 2). Eight lines are observed from interaction of the unpaired-electron spin with ^{59}Co ($I = 7/2$, 100% abundant). The linewidths are anisotropic and depend upon the spin state of the cobalt. This is a well characterized phenomenon found in many other transitional complexes where $S = \frac{1}{2}$ and nuclear hyperfine structure is observed.[12] The relaxation time

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[11] R. C. Bray, 'Rapid Mixing and Sampling Techniques in Biochemistry,' Academic Press, New York, 1964, 195.

[12] H. M. McConnell, *J. Chem. Phys.*, 1956, **25**, 709; R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, 1960, **33**, 1107.

for the components of the nuclear fine splitting are predicted to obey the equation: [13]

$$1/T_2 = \mathrm{A} + \mathrm{B}m_I + \mathrm{C}m_I^2 \qquad (1)$$

where m_I is the spin state of the nucleus and T_2 the spin–spin relaxation time. A, B, and C are constants dependent on the anisotropy in g and A, and also on the correlation time for molecular tumbling, τ_c. Lowering the sample temperature causes the spectra to become more anisotropic since the coefficients of m_I and m_I^2 depend upon τ_c, which in turn depends on the viscosity of the solvent. At Q-band, spectra are not observed, probably due to the dependence of the first two terms on the magnetic field, *i.e.*, the lines broaden on increasing the magnetic field.

TABLE 2

Hyperfine interaction and g values for $\mathrm{Co(CNR)_6}^{2+}$ and various six-co-ordinate cobalt(II) complexes

R (complex)	Band	$g_\perp$	$g_\parallel$	A (G)	B (G)	g (soln.)	A_i soln. (G)	$\frac{1}{3}(g_\parallel + 2g_\perp)$	$\frac{1}{3}(A + 2B)$ (G)
Me	X	2·09 ± 0·01			75 ± 5	2·055	24·6	(2·06)	
	Q				Broad line				
Et	X	2·089			72·1	2·067	23·95	2·061	
	Q	2·0795	2·0053	63·8	70·0			2·055	25·4
C_6H_{11}	X	2·155			70·7	2·067	25·4	2·078	
	Q	2·0946	2·0049 2·0082 2·0116	62·3	67·3			2·063	24·1
Ph	X	2·083			74	2·059	28 ± 3	2·064	
	Q	2·077	2·005	64·5	71·5			2·053	26·2
$\mathrm{Co(CNMe)_5(MeOH)}^{2+}$	X	2·044	2·00		74	2·0715		2·03	
$\mathrm{Co(CNEt)_5(MeOH)}^{2+}$	X	2·058	2·00	(78)	75	2·0765		2·04	
$\mathrm{Co(CNPh)_5(H_2O)}^{2+}$	X	2·0865	2·00	73	70	2·0796		2·064	22
	Q	2·0755	2·003	79·5	73·6	2·06		2·050	28·1
$\mathrm{Co(CNEt)_5\,py}^{2+}$	X	2·093	2·00	(80)	70·2	2·062	17·5	2·062	
$\mathrm{Co(CNMe)_4Cl_2}$	X	2·090	2·005	65·7	74·9	2·118	13·2 (^{35}Cl and ^{37}Cl?)	2·062	27

At 77°K, frozen solutions show that the g tensor has two components. Measurements were made at Q-band since, despite the higher probe temperature, the spectra were better resolved in the higher magnetic field. The spectra were analysed on the basis of a first-order interaction with the magnetic field, the regular separation of the components shows that this is valid within the accuracy of the experiment. The spectrum of $\mathrm{Co(CNMe)_6}^{2+}$ does not show well resolved ^{59}Co structure at either X- or Q-Band. A temperature study of this system showed that the component lines become broader on increasing the temperature. It is possible that some form of molecular motion is still present in the methyl isonitrile glass at 77°K. The spectrum of $\mathrm{Co(CNC_6H_{11})_6}^{2+}$ shows additional fine structure on both g components. This may be due to the complex having different conformational isomers, or possibly to a mixture of differently co-ordinated complexes (see later). Considerable steric interference between the bulky cyclohexyl groups may be expected.

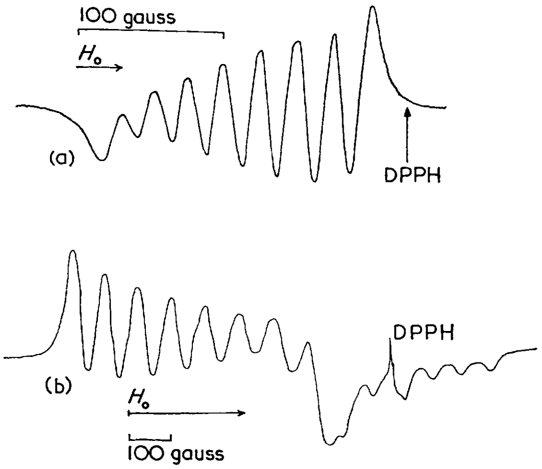

FIGURE 1 E.s.r. spectra of (a) $\mathrm{Co(CNEt)_6}^{2+}$ in CNEt at 293°K (X-band); (b) $\mathrm{Co(CNEt)_6}^{2+}$ in CNEt glass at 150°K (Q-band)

$\mathrm{Co(CNR)_5}^{2+}$.—The spectra of these complexes are very dependent on the solvent, and to a lesser extent on the ligand. In solvents such as dichloromethane and chloroform the complexes have a single resonance at g 2·09. It is sometimes rather asymmetric. In water (only the alkyl isonitriles are soluble), methanol, acetonitrile, nitromethane, and similar polar solvents, solution spectra show two broad overlapping asymmetric lines at g *ca.* 2·08 and 2·14, again with no resolved structure. The presence of water or alcohol causes decomposition of the complexes to a yellow diamagnetic product which is mainly the $\mathrm{Co(CNR)_5}^{+}$ complex. The paramagnetic solutions are green to yellow coloured, depending on the solvent and the temperature. The glass spectra at 77°K are particularly complex in those solvents which show two lines at room temperature due to overlap of the different components.

$\mathrm{Co(CNPh)_5}^{2+}$.—(Table 3, Figure 2). This complex has two forms in the solid state.[5] A blue-green complex $\mathrm{Co(CNPh)_5(H_2O)(ClO_4)_2}$ is precipitated from alcohol solutions of $\mathrm{Co(ClO_4)_2,6H_2O}$ by addition of phenyl isonitrile. Drying this complex under high vacuum gives a yellow complex $\mathrm{Co(CNPh)_5(ClO_4)_2}$. Both complexes form green solutions in dry methylene chloride. Their visible spectra show an absorption at 14,400 cm.$^{-1}$ (ε 290) and a slight shoulder at 22,000 cm.$^{-1}$. At room temperature the e.s.r. spectra have very asymmetrical resonances with a very slight difference in their solution g values. Over a period

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[13] A. Carrington and A. D. McLachlan, 'Introduction to Nuclear Magnetic Resonance,' Harper & Row, New York, 1967, chap. 11.

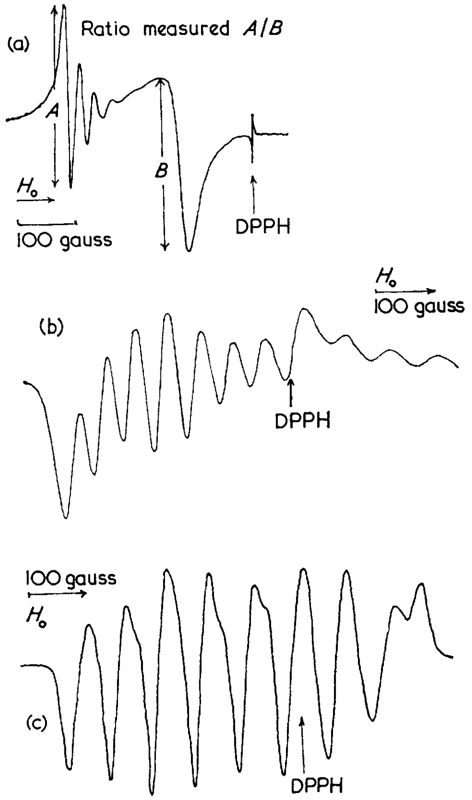

FIGURE 2 E.s.r. spectra (a) the yellow form of $Co(CNPh)_5^{2+}$ in CH_2Cl_2 after 3 days (*X*-band); (b) $Co(CNEt)_5^{2+}$ in CH_2Cl_2 glass at 77°K (*X*-band), characteristic of all the five-co-ordinate isonitrile complexes; (c) $Co(CNPh)_5(H_2O)^{2+}$ in wet CH_2Cl_2 at 77°K (*X*-band), characteristic of all the six-co-ordinate complexes

of days additional lines appear in the spectra of solutions of the yellow complex at *g* 2·140 with a fine splitting of *ca.* 27 G. They also appear, but are of lower intensity, in methylene chloride solutions of the blue complex [Figure 2(a)]. They are not observed in polar solvents. Four lines can be easily distinguished and a fifth discerned under favourable conditions. This is thought to be ^{59}Co splitting rather than ^{35}Cl and ^{37}Cl splitting (from interaction with a molecule of solvent) since the same group of lines appear in methyl bromide and in chloroform solutions. E.s.r. spectra were measured concurrently with visible spectra; as the *g* 2·14 signals increase relative to the *g* 2·08 signal, the absorption at 14,400 cm.$^{-1}$ decreases and the shoulder at 22,000 cm.$^{-1}$ increases. The intensity of the *g* 2·14 signals depend upon water present. This may be connected with the easy reduction of $Co(CNPh)_5^{2+}$ to $Co(CNPh)_5^{+}$ in wet methylene chloride. The reaction observed is possibly:

$$Co(CNPh)_5^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CNPh)_4^{2+} + CNPh$$

The isonitrile is probably removed by some subsequent decomposition, but the reaction is of a rather complex nature; further studies were not made. Thus the structured signal is attributed to the four-co-ordinate species. Adding small quantities of *p*-tolyl isonitrile to the solution causes the immediate ($\leqslant$2 min.) disappearance of the signals at *g* 2·14 which supports the equilibrium theory. It was also found that the ratio of the sizes of the *g* 2·14 and 2·08 resonances does not start at zero at the time origin, showing that some of the four-co-ordinate complex is initially present (the peak-to-peak linewidth of the signals remains constant throughout). It was found that this initial ratio depended upon the length of time for which the sample was pumped under high vacuum. Pumping at 60°C for a week caused it to increase to 1·0. The amount of the four-co-ordinate complex does not increase indefinitely but levels off at a ratio of about 2·0. On the basis of the visible spectra, up to 30% of $Co(CNC_6H_5)_4^{2+}$ may then be present.

Both the blue-green and the yellow forms of the complex remain green in methylene chloride glasses at 77°K. The spectra are complicated by the formation of the four-co-ordinate complex, so that measurement must be made on fresh solutions, and the yellow complex must not be dehydrated for too long. Spectra are characterised by two *g*-components whose separation is such that they can be analysed from the *X*-band spectra. The *g* components have a much greater separation than those of the six-co-ordinate complexes. It was found that if a solution of methylene chloride saturated with water was used to form the glass there was a dramatic change in the spectrum [Table 2, Fig. 2(c)], when it becomes very similar to those of the $Co(CNR)_6^{2+}$ complexes in that the separation between $g_\parallel$ and $g_\perp$ decreases. The glass also becomes a strong yellow colour on freezing, but the green colour is restored on warming up the sample. The change is totally reversible. These observations may show that a water molecule is forced into the sixth position of the co-ordination sphere of the cobalt as a result of a contraction in the glass on freezing. Since solutions of the blue-green complex do not show this phenomenon, it is likely that the water molecule is not co-ordinated in this complex in methylene chloride solution.

$Co(CNR)_5^{2+}$ (R = Me, Et, or C_6H_{11}—(Table 3, Figures 2 and 3.) The dimer which forms in the solid state dissociates in methylene chloride solution to form the five-co-ordinate species. These have a symmetrical signal

TABLE 3

Hyperfine interaction and *g* values for $Co(CNR)_5^{2+}$ in methylene chloride

R (complex)	Band	$g_\perp$	$g_\parallel$	*A* (G)	*B* (G)	*g* (soln.)	Width soln.: (G)	$\frac{1}{3}(g_\parallel + 2g_\perp)$	$\frac{1}{3}(A + 2B)$ (G)
Me	*X*	2·1227	(2·0115)	77·2	59	2·0981	30	2·086	14
Et	*X*	2·1275	2·0064	80·2	50·3	2·093	29·2	2·087	7
C_6H_{11}	*X*	2·1160	2·0061	78	54	2·09		2·081	10
Ph	*X*	2·118	2·004	86	50	2·081	45	2·08	5
	Q	2·0982 * 2·1787	2·004	80				2·117	

* Two asymmetric lines are observed.

at *g* 2·09. The solutions do not show any signal from the formation of $Co(CNR)_4^{2+}$. The effect of the addition of small quantities of other ligands, such as pyridine, was studied. Thus for a 2×10^{-3}M-solution of $Co(CNEt)_5^{2+}$, as the concentration of pyridine is increased, the signal broadens and fine structure eventually appears. At a molar ratio pyridine : complex of 10 : 1 three overlapping spectra are discernible. When the ratio is increased to 100 : 1 there is increased fine structure with more than eight component lines. It is likely that three complexes are present: $Co(CNEt)_5^{2+}$ (*g* 2·093), $Co(CNEt)_5\,py^{2+}$ (*g* 2·062, *A* = 17 G), and $Co(CNEt)_4\,py_2^{2+}$ (*g ca.* 2·1, *A ca.* 27 G). at 77°K with added pyridine is very dramatic [Fig. 3(b)]. At ⩽2M excess of pyridine the spectrum of $Co(CNEt)_5^{2+}$ is replaced by that of $Co(CEt)_5\,py^{2+}$. Further increase of the pyridine concentration causes the component lines to split (attributed to a mixture of $Co(CNEt)_5\,py^{2+}$ and $Co(CNEt)_4\,py_2^{2+}$). Finally when the predominant species is probably $Co(CNEt)_4\,py_2^{2+}$, at high pyridine concentrations, the structure becomes well resolved. The structure probably comes from coupling between the unpaired electron and ^{14}N in the pyridine. In order to obtain the spectrum of the $Co(CNEt)_4\,py_2^{2+}$ ion, the complex $[Co(CNEt)_4]Br_2$ was dissolved in a solution of pyridine and methylene chloride. Although ^{79}Br and ^{81}Br splitting is observed in the solution spectra, when the solutions are frozen a spectrum showing ^{14}N coupling is obtained (see later Discussion).

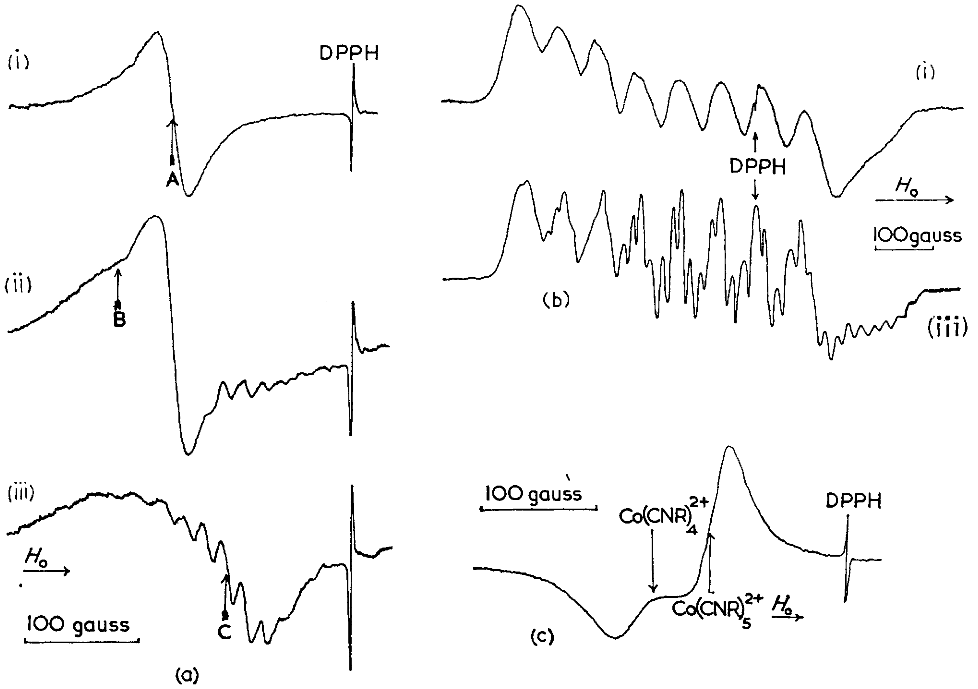

FIGURE 3 E.s.r. spectra of 2×10^{-3}M-$Co(CNEt)_5^{2+}$ in CH_2Cl_2 at (a) 293° (*X*-band) and (b) 77°K (*X*-band) in solutions containing i, 2×10^{-3}; ii, 2×10^{-2}; and iii, 2×10^{-1}M-pyridine. A, B, and C represent the approximate positions of the complex species $Co(CNR)_5^{2+}$, $Co(CNR)_5\,py^{2+}$, and $Co(CNR)_4\,py_2^{2+}$. (c) E.s.r. spectra of $Co(CNPh)_5^{2+}$ in methyl cyanide at 293°K (*X*-band)

At higher concentrations of pyridine the spectra broaden again and ultimately disappear, probably owing to the further replacement of isonitriles, and the cobalt changing to a high-spin state (cf. ref. 14). Cooling a sample to 250°K causes the fine structure to disappear, whilst heating to 320°K causes some broadening of the lines. This dependence on temperature is probably due to both an increase in the viscosity of the solvent with lowering temperature, whilst on increasing the temperature, exchange of the pyridine ligands between different complexes becomes more significant. An exchange time of *ca.* 10^{-8} sec. would be needed for this process.

At 77°K the glass spectra of the $Co(CNR)_5^{2+}$ ions are characterised by two *g*-components, and are very similar to the spectra of the yellow form of $Co(CNPh)_5^{2+}$ in dry methylene chloride glass. However, methylene chloride glasses saturated with water do not show any change from those prepared in dry methylene chloride, showing that a water molecule is not co-ordinated under these conditions.

The change in the spectra of methylene chloride glasses

The visible spectra of solutions of $Co(CNEt)_5^{2+}$ in methylene chloride at varying pyridine concentration do not show isobestics. The most characteristic change is the appearance of a very strong absorption at 23,900 cm.$^{-1}$, the size of which and the rate at which it increases depending on the pyridine concentration. The absorption from $Co(CNEt)_5^{2+}$ at 13,000 cm.$^{-1}$ broadens, and at intermediate pyridine concentrations is replaced by a weaker one at 16,500 cm.$^{-1}$ with a shoulder at 17,400 cm.$^{-1}$.

The e.s.r. spectra in solvents other than methylene chloride are complicated by the mixture of species present. Data for some of the complexes are shown in Table 2, the spectra were analysed on the assumption that the main species was $Co(CNR)_5S^{2+}$ (S = solvent). The solution spectra show that in most polar solvents there is a

[14] D. L. Williams, D. W. Smith, and R. C. Stoufer, *Inorg. Chem.*, 1967, **6**, 590.

considerable concentration of the $Co(CNR)_4S_2^{2+}$ ion. [Although it is possible to distinguish several species, it is not possible to say whether they represent $Co(CNR)_4S^{2+}$, $Co(CNR)_4S_2^{2+}$, or $Co(CNR)_5S^{2+}$. However, the latter can be fairly safely distinguished by using a low concentration of L in an inert solvent such as methylene chloride]. These observations are in agreement with previous work on solutions of $Co(CNMe)_5^{2+}$ in water, where it was shown that in the visible spectrum the band at 14,500 cm.$^{-1}$ does not obey Beer's Law,[2] indicating that the solutions contain species other than the five-co-ordinate complex.

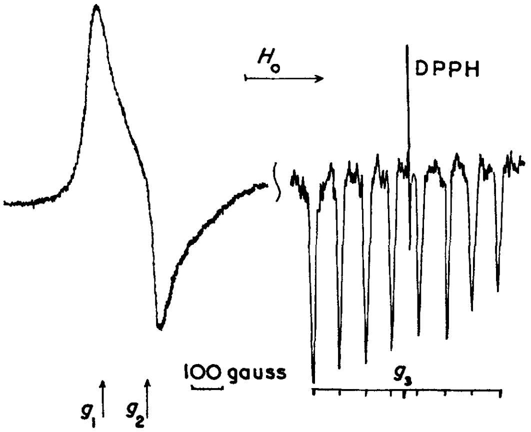

FIGURE 4 E.s.r. spectra of $Na_3Co(CN)_5$ in methanol at 150°K (Q-band)

$Co(CN)_5^{3-}$.—(Table 4, Fig. 4). The spectrum of this ion has been reported in an ethylene glycol–water glass at 77°K.[6] The spectra obtained in methanol and in the rapidly frozen aqueous solutions were similar to this, although slightly different g values were obtained, in particular $g_{\parallel}$ is slightly $>2{\cdot}0023$. The spectra appear to be independent of the cyanide concentration. The rate of the dimerisation reaction is evidently very dependent on the medium, and and it is possible that it is affected by ion-pair formation. Strong ion-pairing would be expected in the high ionic-strength solutions used in the quenching experiment, and in non-aqueous solvents. A rough estimate of the rate in 3M-sodium cyanide solution, from the quenching experiment, gives a second-order rate constant of 10^5—10^6 l. mole.$^{-1}$ sec.$^{-1}$.

TABLE 4

Hyperfine interaction and g values for $Co(CN)_5^{3-}$

Solvent	Band	Co:CN	g (soln.)	$g_{\parallel}$	$g_{\perp}$	$\frac{1}{3}(g_{\parallel} + 2g_{\perp})$	A	B	$\frac{1}{3}(A + 2B)$
MeOH	X	1:16	2·115	2·006	2·156	2·106	87·4	28·6	9·3
		1:6·8	2·115	2·009	2·155	2·107	89·2	30·0	9·7
	Q	1:6	2·103	2·0004	2·137 2·166	2·101	85·2		
H_2O..........................	X	3M-NaCN	2·11	2·005	2·161	2·109	88·5	29·8	9·6
		2·5M-$NaClO_4$	2·11	2·005	2·158	2·106	90	28	11

Careful examination of the spectra at X-band shows that the components on $g_{\perp}$ are not regularly spaced. This is not due to either a second-order splitting dependent on the magnetic field, or to overlap of the $g_{\parallel}$ components. At Q-band the eight $g_{\parallel}$ components are completely separated from $g_{\perp}$, however the $g_{\perp}$ components have collapsed, and the single line obtained seems to be formed from two components. This suggests that either: (a) the complex does not have strictly C_{4v} symmetry, but is C_{2v}, since two of the planar cyanides could be bent downwards out of the plane (if they could be bent down by 30° then the trigonal bipyramidal structure is obtained, which seems unlikely from the g values) or, (b) there is also a small quantity of $Co(CN)_4^{2-}$ (or a solvated species), which might explain the much greater intensity of the component on $g_{\perp}$ at lowest field in the X-band spectra, and is also in harmony with recent visible spectra work.[8]

The reason for the collapse of the components on $g_{\perp}$ at Q-band is not obvious. Variation of the temperature at X-band between 77 and 165°K shows no observable change in the spectrum, which seems to indicate that the collapse is not due to some form of motion in the glass at the higher temperature of the Q-band. The effect may possibly be due to higher magnetic field of the Q-band. The spectra of some $Co(CNR)_5^{2+}$ complexes also show collapse of the $g_{\perp}$ components at Q-band.

$Co(CNR)_4X_2$ ($R = Me$, Et, C_6H_{11}, p-tolyl; $X = Cl$, Br, or I).—(Table 5, Figure 5). The solution spectra are characterised by well resolved, but asymmetric, hyperfine coupling between cobalt and the halogen.[15] For ^{127}I, $I_z = 5/2$ we expect eleven lines in the ratios $1:2:3:4:5:6:5:4:3:2:1$, for ^{79}Br and ^{81}Br, $I_z = 3/2$, we expect seven lines in the ratios $1:2:3:4:3:2:1$, and for ^{35}Cl and ^{37}Cl, $I_z = 3/2$ we should also expect seven lines. The observed intensities are considerably distorted from these calculated ratios, probably because of variations in the linewidths with the spins of the cobalt and the halogen, for each individual component. Since the cobalt splittings are not resolved this will considerably alter the peak-to-peak intensity of the derivative spectra; this is consequently not an accurate measurement of the intensity. For the bromide and iodide complexes the spectra are less distorted in solvents such as benzene and methylene chloride than they are in alcohols.* For the chloride complexes in methylene chloride the fine structure is ill resolved, and it is possible that it is due to ^{59}Co, or a mixture of ^{59}Co and ^{35}Cl–^{37}Cl splittings. More than seven components can be resolved under favourable conditions. In water and in alcohols complexes such as $Co(CNMe)_4Cl_2$ appear to disproportionate to form, $e.g.$ $Co(CNMe_3)_5^{2+}$.

The addition of lithium bromide or iodide to alcohol solutions of the bromide and iodide complexes causes a slight broadening of the hyperfine structure; this is probably due to a change in the viscosity of the solvent rather than to chemical exchange.[12] Addition of pyridine to $Co(CNEt)_4Br_2$ or $Co(CNC_6H_4Me)_4Br_2$ (or the iodides)

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* Computor calculations of simulated spectra are in progress to clarify this issue.

[15] J. P. Maher, *Chem. Comm.*, 1967, 632.

does not affect the hyperfine structure up to molar ratios of 100 : 1 in pyridine.

Hyperfine splitting from ^{59}Co is sometimes just resolvable on the component lines in the bromide and iodide complexes. It is most pronounced in alcohol and acetone solutions, and throughout all the spectra gives the lines a very asymmetric appearance. It is about 15 G in size.

At 77°K the glass spectra are too complex to analyse, since hyperfine splitting from both the halogen and the cobalt give irregular spectra. However the spectrum of Co(CNMe)$_4$Cl$_2$ in a methylene chloride glass is typical for a cobalt in D_{4h} symmetry, showing only ^{59}Co components on both g components. Any ^{35}Cl and ^{37}Cl splitting must be <1 G, the spectrum being very similar to that for Co(CNPh)$_5$(H$_2$O) [Figure 2(c)]. This suggests that the chlorine is very much more ionic than the bromine and iodine in their compounds. There is however a considerable difference in the solution g-value (2·118) and that calculated from $1/3(g_{\parallel} + 2g_{\perp})$, which is greater than the experimental error and shows that there is a difference in the manner in which the chloride is complexed in solution and in the glass. A similar effect is noted in frozen solutions of Co(CNEt)$_4$Br$_2$ in methylene chloride containing a 100 : 1 molar ratio of pyridine. In solution ^{79}Br and ^{81}Br splitting is unaffected, although in the glass the spectrum shows only ^{59}Co and ^{14}N splitting [Figure 5(b)]. Five components in the ratio 1 : 2 : 3 : 2 : 1 would be expected from two equivalent ^{14}N, ($I_z = 1$). Whereas the solutions at room temperature are green, the frozen solutions are a brick red, possibly due to a charge-transfer interaction between the pyridine and the cobalt. For this spectrum $A_{\perp}(^{14}\text{N}) = 17$, $A_{\perp}(^{59}\text{Co}) = 65$—$70$ G.

TABLE 5

Hyperfine interaction and g values for Co(CNR)$_4$X$_2$

Complex		g				A· (G)		
		CH$_2$Cl$_2$	C$_6$H$_6$	Other solvents	Solid	CH$_2$Cl$_2$	C$_6$H$_6$	Other solvents
(MeNC)$_4$Co	Cl$_2$	2·118		2·067/2·128 [a] *	2·109 †	13·2		
	Br$_2$	2·097		2·089 [b]; 2·078 [a] *	2·068 †	73·7		74·7 [b]; 72·9 [a]
	I$_2$	2·064			2·054 †	95·6		
(EtNC)$_4$Co	Cl$_2$	2·104		2·07/2·122 [a] *				14 [a]
	Br$_2$	2·100		2·086 [b]	2·067 †	74·7		73·4 [b]; 71 [a]
	I$_2$	2·068	2·039			91·6	93·3	
(C$_6$H$_{11}$NC)$_4$Co	Cl$_2$	2·110				14		
	Br$_2$	2·100	2·075	2·087 [b]; 2·076 [a]	2·095	72·5	69·7	76 [b]; 72 [a]
	I$_2$	2·069	2·046	2·053 [b]; 2·071 [a]	2·057	95·1	89·6	94 [b]; 90·8 [a]
(p-MeC$_6$H$_4$·NC)$_4$Co	Cl$_2$	2·094	2·080	2·115 [b,c]			20	19 [c]
	Br$_2$	2·075			2·092	69·4		
	I$_2$	2·044	2·071		2·063	92·9	(97·5)	

* Two overlapping signals. † Asymmetric signal, the measurement was taken to where the signal crosses the base-line position of the derivative curve.

[a] In ethanol. [b] In acetone. [c] In methanol.

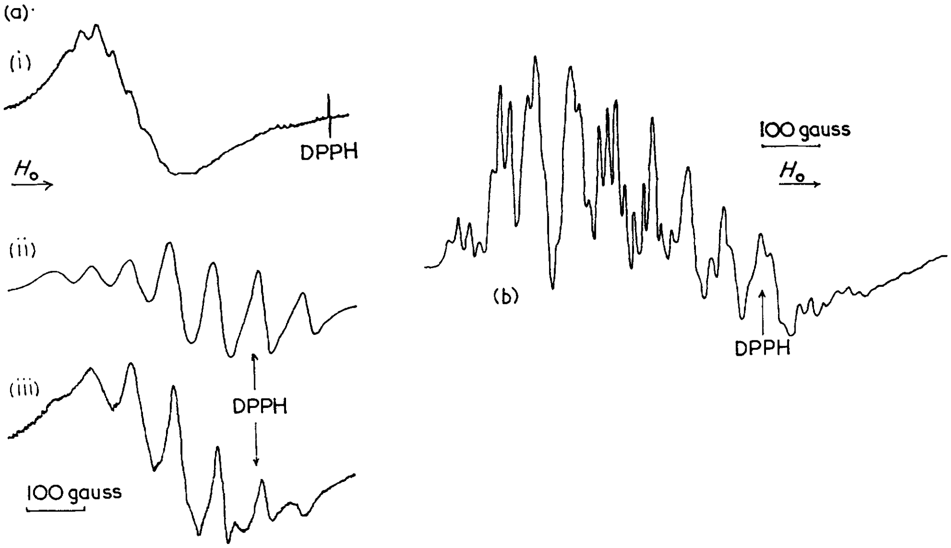

FIGURE 5 E.s.r. spectra of (a) i, Co(CNMe)$_4$Cl$_2$ in CH$_2$Cl$_2$; ii, Co(CNC$_6$H$_4$Me)$_4$Br$_2$ in benzene; and iii, Co(CNC$_6$H$_4$Me)$_4$Br ethanol, (X-band) at 293°K; and (b) Co(CNC$_2$H$_5$)$_4$Br$_2$ in CH$_2$Cl$_2$–pyridine, (X-band) at 77°K

In solution the paramagnetic molecules are tumbling rapidly and randomly so that only the average g value, which is equal to 1/3 of the trace of the g tensor, *i.e.*, $1/3(g_{xx} + g_{yy} + g_{zz}) = 1/3(2g_{\perp} + g_{\parallel})$, is obtained. Unless there is a good correlation between the solution and the solid-state g-values, calculated in this way, it is incorrect to infer the solution structure from the glass spectra. Comparison of the Tables shows that for the ions Co(CNR)$_5$$^{2+}$,

$Co(CNR)_6^{2+}$, and $Co(CN)_5^{3-}$ there is a good correlation between the solution and the solid-state values, whereas for $Co(CNPh)_5(H_2O)^{2+}$ (compared with the solution of the blue complex in wet methylene chloride), $Co(CNMe)_4Cl_2$, and $Co(CNEt)_4Br_2$ (in pyridine–methylene chloride) there is not shown a good correlation. For these last three there is probably some structural change at low temperature.

In a like manner the solution hyperfine coupling A_i is $1/3(A + 2B)$; the measured couplings show that A and B are of opposite sign. The correlation between the solution and solid-state values is very good for $Co(CNR)_6^{2+}$ ions. Values of A_i may be calculated for the $Co(CNR)_5^{2+}$ and $Co(CN)_5^{3-}$ ions from the glass spectra. It is probably safe to assume that A and B still have opposite signs in these.

DISCUSSION

The behaviour of the components of the g and A tensors for low-spin cobalt complexes in D_{4h} and C_{4v} symmetry have been described[16] in terms of the four irreducible components of the $3d$ orbitals on the cobalt; $|0\rangle$, $|\varepsilon\rangle$, $|\mu\rangle$, and $(|-1\rangle, |1\rangle)$ where $|\varepsilon\rangle = 1/\sqrt{2}\ (|2\rangle + |-2\rangle)$; $|\mu\rangle = 1/\sqrt{2}\ (|2\rangle - |-2\rangle)$. The $|\varepsilon\rangle$ orbital will be highest in energy, thus the unpaired electron can be in the $|0\rangle$, $|\mu\rangle$, or $(|-1\rangle, |1\rangle)$ orbital. For the last the g values would be $g_\parallel = 4$, $g_\perp = 0$. These differ greatly from the experimental values, and even if they were drastically modified by strong covalent bonding it would still be expected that $g_\perp < 2$. Calculation of the g tensor to first order gives, for the electron in $|0\rangle$, $g_\parallel = 2{\cdot}0$ and $g_\perp = 2{\cdot}0 + 6\ (\zeta/E_1)$, and for the electron in $|\mu\rangle$, $g_\parallel = 2 - 8(\zeta/E_2)$ and $g_\perp = 2 + 2(\zeta/E_3)$, where E_1, E_2, and E_3 refer to the energy separations $(|-1\rangle, |1\rangle)$ to $|0\rangle$, $|\mu\rangle$ to $|\varepsilon\rangle$, and $(|-1\rangle, |1\rangle)$ to $|\mu\rangle$ respectively. For cobalt, the spin–orbit coupling constant ζ will be *ca.* 400 cm.$^{-1}$.[16]

In D_{3h} symmetry three irreducible components of the cobalt $3d$ orbitals are obtained, these are $|0\rangle$, $(|2\rangle, |-2\rangle)$ and $(|1\rangle, |-1\rangle)$. The $|0\rangle$ orbital would be expected to be highest in energy. For the unpaired electron in $(|1\rangle, |-1\rangle)$ $g_\parallel = 4$ and $g_\perp = 0$; if the electron is in $(|2\rangle, |-2\rangle)$ $g_\parallel = 6$, and $g_\perp = 0$, both in first order. Although these values might be modified by a Jahn–Teller distortion and by covalent bonding, they are sufficiently far from the observed values to show that the $Co(CNR)_5^{2+}$ species are not trigonal bipyramidal in the glasses at 77°K.

Thus from the theoretical g-values it seems likely that the unpaired electron is in $|0\rangle$ rather than $|\mu\rangle$ since the latter predicts that one of the g-tensor components should be <2 (*ca.* 1·9 if the rather large value of 30,000 cm.$^{-1}$ was assumed for E_2). If the unpaired electron is in the $|0\rangle$ orbital, then the components of the hyperfine coupling A and B are given approximately by,[16]

$$A = P[-\kappa + 4/7 - (6/7)f] \qquad (2)$$
$$B = P[-\kappa - 2/7 + (45/7)f]$$

where $P = 2\gamma\beta\beta_{Co}\langle r^{-3}\rangle$, κ is proportional to the square of the coefficient of the $4s$ orbital and to $\psi_{4s}(0)^2$ and can be associated with the ligand-field mixing $3d^64s$ into $3d^7$,[17] and $f = \zeta/E_1$. Values of P and κ appropriate to Co are 0·022 cm.$^{-1}$ and 0·2—0·3 respectively.[18]

If average values for the g and hyperfine couplings are taken, and it is assumed that P is constant for the different complexes (a value of 0·017 cm.$^{-1}$ is appropriate to the data), the ratio A/B (which is negative), together with the spectral value of f, gives a measure of κ [Table (6)]. The κ values are considerably lower for the five- than for the six-co-ordinate isonitrile complexes, which means that there is much less tendency to mix the $3d$ and $4s$ orbitals of the cobalt in the latter. Since the extent of this mixing will depend on the geometry of the complex, and will be larger with less regular complexes, this is consistent. It gives a method for distinguishing those complexes which are genuinely five co-ordinate. The value of κ for the $Co(CN)_5^{3-}$ ion is very low in comparison with those for the isonitrile complexes. Although it would be strictly necessary to obtain the spectrum of an ion $Co(CN)_5S^{3-}$ for comparison, this suggests that this species is five-co-ordinate in solution, as in the solid state. Any association with a water molecule is only very weak.

TABLE 6

Values of κ and f calculated for the isonitrile complexes

Complex	κ	f
$Co(CNR)_5^{2+}$	0·123	0·0202
$Co(CNR)_6^{2+}$	0·196	0·0120
$Co(CNR)_5S^{2+}$	0·175	0·0110
$Co(CNPh)_5^{2+}$	0·102	0·0175
$Co(CNPh)_6^{2+}$	0·200	0·0130
$Co(CNPh)_5(H_2O)^{2+}$	0·200	0·0140
$Co(CN)_5^{3-}$	0·046	0·0260
$Co(CNMe)_4Cl_2$	0·208	0·0150

S = solvent.

In comparison with the hyperfine couplings in various hydrated cobalt salts,[18] the couplings in the isonitrile complexes and in $Co(CN)_5^{3-}$ are very much smaller. This indicates considerable covalent character in the complexes and shows that the unpaired electron is delocalised on the ligands to a considerable extent, a representation of the bonding as ionic is thus likely to be rather inaccurate. Although isotropic coupling constants are not resolved for the $Co(CNR)_5^{2+}$ complexes they may be estimated from the glass spectra. They are generally much less than the couplings in the $Co(CNR)_6^{2+}$ and $Co(CNR_5)S^{2+}$ complexes, indicating a more covalent bonding in the five- than in the six-co-ordinate complexes.

The solutions and glasses change colour from green to yellow whenever the complexes change from the five- to the six-co-ordinate form. This colour change is also observed on removal of the water from $[Co(CNPh)_5(H_2O)](ClO_4)_2$. In solution the yellow colour

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[16] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[17] J. S. Griffith, 'The Theory of Transition-Metal Ions,' Cambridge University Press, Cambridge, 1961.

[18] A. Abragam and M. L. H. Pryce, *Proc. Roy. Soc.*, 1951, *A* **206**, 173.

is associated with the appearance of a very strong absorption in the near u.v. (probably a charge-transfer absorption), whilst the absorption between 14,000 and 10,000 cm.$^{-1}$ disappears. A tentative explanation of the change in the $g_\perp$ values between the six- and the five-co-ordinated complexes, and of the colour change, may be given in terms of simple geometry changes.

The five-co-ordinate complex may have a structure in which the cobalt atom lies above the plane of the equatorial ligands [Figure (6), $\theta > 90°$], under certain conditions this structure can flatten out ($\theta = 90°$), either by the co-ordination of another group, *e.g.* water, or, as in $[Co(CNPh)_5(H_2O)](ClO_4)_2$, by a solid-state effect. As long as the sixth ligand has a relatively weak ligand field, the ligand field of the cobalt will be dominated by that of the five isonitrile groups, and a simple ligand-field calculation gives the effect of varying θ from 90—120° upon the relative positions of the *d* orbitals.[17] * If the unpaired electron is in $|0\rangle$, then the decrease in $g_\perp$ on flattening out the complex reflects a change in E_1 from 20,000—30,000 cm.$^{-1}$. This would correspond in the calculation to a change in θ from 105 to 90°. Such a change also requires a shift of the 14,000 cm.$^{-1}$ absorption to 18,000—19,000 cm.$^{-1}$, since this may tentatively be assigned to the $^2A_1 \rightarrow {}^2B_1$ transition.[6] Since the separation of $|0\rangle$ and $|\varepsilon\rangle$ would be decreased by a group in the sixth position, the absorption would be shifted to slightly longer wavelength. [A weak absorption appeared at ~17,000 cm.$^{-1}$ in solutions of $Co(CNEt)_5{}^{2+}$ in methylene chloride containing pyridine, where the predominant complex is probably $Co(CNEt)_5\,py\,{}^{2+}$.] Since in the solid state the yellow form of $Co(CNPh)_5{}^{2+}$ is created by the removal of a water molecule, rather than by its co-ordination, a geometry change of this type is an attractive explanation (there is no evidence for the co-ordination of one of the perchlorate groups in this system [2]). The calculation is claimed to be no more than a qualitative explanation and a similar effect might be created by changing θ for just two of the ligands, which would put the structure intermediate between a trigonal bipyramid and a square pyramid. Most of the complexes apparently have C_{4v} symmetry, although there is some evidence for C_{2v} symmetry in $Co(CN)_5{}^{3-}$.

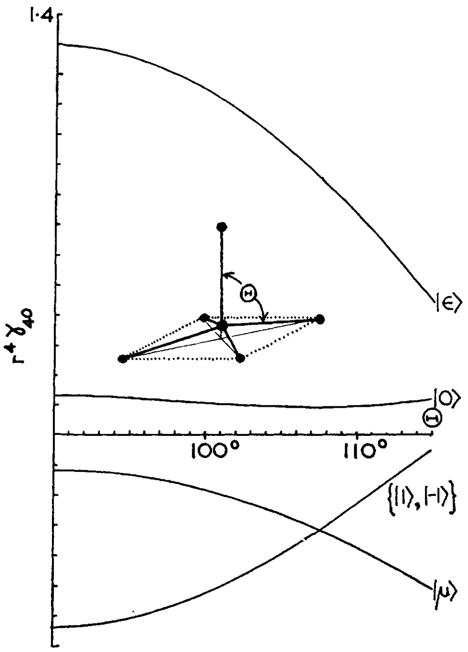

FIGURE 6 The effect of the variation of the angle between the axial and the equatorial ligands (θ) on the ligand field for square pyramidal co-ordination (measured in proportion to the quartic term)

Alternatively, we can consider the effect of bringing in a sixth ligand to closer co-ordination. For the series $Co(CNPh)_4{}^{2+}$, $Co(CNPh)_5{}^{2+}$, and $Co(CNPh)_6{}^{2+}$ (Table 7) the differences in the $g_\perp$ values are adequately explained by considering a planar form for $Co(CNPh)_4{}^{2+}$, and then adding two more isonitrile groups in the fifth and sixth positions, each isonitrile group causing an increase of 8500—9000 cm.$^{-1}$ in the separation of $|0\rangle$ and $(|-1\rangle, |1\rangle)$. A decrease in $g_\perp$ for cobalt phthalocyanine is observed on co-ordinating pyridine or quinoline in the fifth and sixth positions.[15] The absorption $^2A_1 \rightarrow {}^2B_1$ should move into the i.r. region on co-ordinating a strong field ligand; since a low-spin octahedral d^7 complex should show a strong Jahn–Teller distortion, the position of this absorption will be a measure of that distortion.

TABLE 7

Collected parameters for the phenyl isonitrile complexes

Complex	*g* (soln.)	$g_\perp$	Sepn. of $|0\rangle$ and $(|1\rangle, |-1\rangle)$ (cm.$^{-1}$)
$Co(CNPh)_4{}^{2+}$	2·140	(2·210)	11,400
$Co(CNPh)_5{}^{2+}$	2·081	2·118	20,400
$Co(CNPh)_6$	2·059	2·083	28,900

The addition of ligands with such drastically differing ligand-field strengths as water, pyridine, and isonitrile has essentially the same effect. This would be rather surprising if the change in $g_\perp$ and the absorption spectra was solely due to the addition of the sixth ligand. Ligand-field calculations of this type are necessarily very qualitative so that the variation of $g_\perp$ probably receives contributions from a change in θ as well as the increased ligand field caused by introducing another group. Changes in the bond lengths and in the covalency of the complexes will also have an effect; smaller and

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* The calculation depends upon the assumed value of the ratio $r^2\gamma_{20}/r^4\gamma_{40}$, *i.e.* the square and the quartic terms when the *d* orbitals are expressed in terms of spherical harmonics. Agreement with previous authors work can be obtained by taking the ratio as 2·6833.[19,20] A dipolar interaction was assumed for the calculation.

[19] C. J. Ballhausen, *Dan. Mat. Fys. Medd.*, 1954, **29**, Part 4.

[20] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' Wiley, New York, 1967.

second-order terms were omitted from this calculation.*

Linewidths of the Solution Spectra.—Those complexes with six-co-ordinated ligands show ^{59}Co splitting if the ligands are strongly co-ordinated. Thus spectra of complexes where the sixth ligand is isonitrile, pyridine, (or triphenylphosphine) show structure, but where it is water, alcohol, alkyl cyanide, or nitromethane, they do not. Similarly spectra of the $Co(CNR)_4{}^{2+}$ and the $Co(CNR)_4X_2{}^{2+}$ complexes in certain solvents show resolution of the ^{59}Co splitting. However, none of the five-co-ordinate complexes shows any fine structure in any of the solvents studied. This may be partly associated with the low isotropic hyperfine splittings predicted for these on the basis of the solid-state data (Table 3).

The peak-to-peak linewidths (in gauss) of the derivative spectra of the complex ions $Co(CNEt)_6{}^{2+}$ and $Co(CNPh)_4{}^{2+}$ at 25° are given respectively by the equations:[21]

$$\text{Width } (CoL_6) = 14{\cdot}5 + 1{\cdot}0m_I + 0{\cdot}25m_I{}^2 \quad (3)$$

$$\text{Width } (CoL_4) = 53 + 21{\cdot}4m_I + 2{\cdot}7m_I{}^2 \quad (4)$$

If it is assumed that τ_c is approximately constant in these complexes then the equation for the linewidths of the five-co-ordinate complexes might be expected to have coefficients in the equation intermediate between those in equations (3) and (4).

In methylene chloride $Co(CNPh)_5{}^{2+}$ shows a single absorption with a peak-to-peak linewidth of 29·2 G, and the linewidths of the other five-co-ordinate complexes are comparable. There is an even greater anisotropy in the g and hyperfine couplings in the ion $Co(CNPh)_4{}^{2+}$ than in $Co(CNPh)_5{}^{2+}$, yet structure is resolved for the former but not for the latter complex. Thus there may be an additional relaxation process for the five-co-ordinate ions in solution. No evidence has been found for the presence of trigonal bipyramidal complexes, but it is possible that a small equilibrium concentration could be present in solution, a rapid transformation between the square pyramidal and the trigonal bipyramidal forms could then shorten T_2 and collapse the ^{59}Co splitting. It is also possible that a rapid variation in θ, caused by solvent exchange on and off the sixth position could have the same effect. The co-ordination of another ligand would freeze either of these processes. The four-co-ordinate complex has fine structure in solvents such as dichloromethane, but this is collapsed in solvents such as alcohols which can co-ordinate to the cobalt. This may also be due to rapid exchange of solvent ligands on and off the fifth and sixth positions. Further, more accurate, calculations on these lineshapes are in progress.

Effects similar to these have been observed in the e.s.r. spectra of some vanadyl acetylacetonate complexes dissolved in solvent mixtures containing benzene and various *N*-heterocyclic bases.[22]

The Tetrakis(isonitrile)cobalt(II) *Dihalides*.[15]—If the unpaired electron is in the orbital, $|0\rangle$ as seems most likely from the data on the other cobalt complexes, then the isotropic solution g-value is given by:

$$g = 2{\cdot}00(1 + 2\zeta/E_1)$$

The contributions to ζ come from both the cobalt and the halogen, as well as from the carbon and nitrogen atoms of the isonitrile ligands. It is possible to subdivide ζ into $\zeta_{\pi\pi}$ and $\zeta_{\sigma\pi}$ representing π–π interaction and σ–π interaction of the metal *d*-orbitals.[23] For $\zeta_{\pi\pi}$ the ligand contribution is positive, for $\zeta_{\sigma\pi}$ it is negative. Since there is a decrease in the isotropic *g*-values, $Cl > Br > I$, in all the complexes, it is likely that the σ–π contributions dominate the g values. This is appropriate for an electron in the $|0\rangle$ orbital as this has σ-symmetry with respect to the halides. From the increasing spin–orbit couplings of the halogens,[24] a much larger change in g than is observed would be expected. The bonding in these complexes is evidently largely covalent so that considerable modification of ζ is to be expected. An analogous effect has been found in some cyclopentadienyl molybdenum and tungsten dihalides.[25]

Comparison of the isotropic hyperfine couplings for the complexes with those of the free halogen atoms [26] enables an estimate to be made of the unpaired electron delocalisation on the halogen. Assuming a coupling for the chlorides of *ca.* 14 G, this gives 8·0, 8·7, and 10·1% as the average extent of the electron delocalisation to the chlorine, bromine, and iodine respectively, showing that with increasing size of the halogen the complexes become more covalent.

I thank Drs. N. S. Hush and J. R. Yandle for valuable discussions and help with the computation, and G. Fothergill for some of the experimental work.

[8/748 *Received, May 28th*, 1968]

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* The e.s.r. spectra of $Co(CNPh)_6{}^{2+}$ and of $Co(CNPh)_5{}^{2+}$ in the presence of various ligands has been reported since this paper was submitted. The observations are similar to those presented here.[21]

[21] N. Kataoka and H. Kon, *J. Amer. Chem. Soc.*, 1968, **90**, 2978.

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